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## Application of the GRI 1.2 Methane Oxidation Model to Methane and Methanol Oxidation in Supercritical Water

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The Gas Research Institute (GRI) has been leading an effort over the past few years to consolidate recent developments in the elementary reaction modeling of the oxidation of methane for combustion applications into a single optimized set of reactions within a standard computational framework. Our interest in the translation of combustion-based models to oxidation in supercritical water has led us to examine the applicability of this mechanism to the low-temperature high-density conditions of supercritical water oxidation at 25 MPa and 400 - 650 °C. This paper shows that the GRI 1.2 mechanism accurately represents the available experimental results on methane over a wide temperature and concentration range. The oxidation of methanol is not well represented by the GRI mechanism when left unchanged. However, if a key modification is made to the reactivity of  $\text{HO}_2$ , good agreement with the methanol oxidation results is achieved. Although designed for conventional combustion conditions, the GRI mechanism can be successfully extended with very little modification to much lower temperature and extreme pressure conditions.

### Introduction

Recently, there have been key developments in reactor design using transpiration-wall technology that mitigate corrosion and scaling issues for applications of supercritical water oxidation (SCWO) to a variety of problematic wastes [1,2]. However, it is likely that a thorough understanding of the operative chemical kinetics for reaction initiation will be required to underpin future applications of this novel design strategy. Continued improvement in reactor design for energy- and cost-efficient operation, and to assure safety will be hampered without better predictive models for the time, temperature, pressure, and concentration dependence of the oxidation process.

Much of the current understanding of the rates and mechanisms of reactions in supercritical water is limited to a small, but growing, list of empirical global expressions for simple chemicals. However, global expressions are of limited use in the formulation of a predictive model. To be valuable as a predictive design tool, a model must be based on at least a quantitative mechanism incorporating the key elementary reaction steps.

The first attempt to use an elementary reaction model to describe the kinetics of oxidation of the simple organics in supercritical water was reported by Webley and Tester [3]. The approach was to modify a successful mechanistic scheme generated for high-temperature gas-phase oxidation for high-density effects on unimolecular reaction rates. This mechanism successfully reproduced the existing methanol oxidation data, but failed to even approximate the experimental results that had been

obtained for methane. Recently, others have developed more extensive elementary reaction models for the oxidation of methane and methanol in supercritical water [4-7]. Similar to the approach in Ref. 3, all of these newer mechanisms have incorporated direct customization of several key reactions for high pressure.

In this paper, we examine the application of the recently developed GRI 1.2 mechanism [8] to the oxidation of methane and methanol at approximately 25 MPa and 420 - 630 °C. This mechanism has high-pressure considerations explicitly included. The goal of this paper is to make a connection between the high-pressure, low-temperature results from recent experiments to the current best effort at representing oxidation of C1 species at combustion conditions. We have adopted an approach that establishes this relationship with the smallest amount of customization as possible, with all of the parameters for both the mechanism and thermodynamics originating from a single well-documented source, and the computation conducted within the framework of a well-established code.

### Methods

The calculations presented here are conducted within the Chemkin II computational framework [9]. The GRI 1.2 mechanism is designed for Chemkin II and is accompanied by a Chemkin-compatible thermodynamic data base. The several calculations reported here using the mechanism of Schmitt [5] use the GRI thermodynamic data base with the addition of properties for  $\text{CH}_3\text{O}_2$ , and several other less important alkyl peroxides, calculated using

THERM [10]. These species are included in the Schmitt mechanism, but not in the GRI data base.

Oxygen is used as the oxidizer at an equivalence ratio of 0.75 for calculations where the stoichiometry is not specifically listed. Moderately lean conditions such as these are likely to be used in industrial SCWO systems.

In some instances, comparison with experiment is done using an effective first-order rate constant,  $k_{\text{eff}}$ , defined as the reciprocal of the time at which the initial fuel mole fraction has fallen to  $1/e$  of its original amount from the expression

$$-d[\text{CH}_4]/dt = k_{\text{eff}} [\text{CH}_4] \quad (1)$$

Thus, much of the emphasis in this paper is on oxidation rates at relatively low conversion. Unfortunately, this paper simultaneously illustrates that these reactions generally are not first order when the fuel concentration is varied over a wide range. Despite this problem,  $k_{\text{eff}}$  is still the simplest way to represent reaction rates when the reaction conditions being considered result in the rates varying by many orders of magnitude.

## Results and discussion

Fig.1 shows a comparison of the results from calculations of the oxidation rate of methane with the presently available experimental data. The results for 390 - 440 °C are calculated from a global fit to dozens of experiments that were conducted at 27 MPa and an initial fuel concentration of 0.1 mol/l [11]. A global fit to these data produces the relationship

$$-d[\text{CH}_4]/dt = k [\text{CH}_4]^{1.84} [\text{O}_2]^{-0.06} \quad (2)$$

where the concentrations are in mol/l,  $k = 10^{17.1} \exp(-30100/T)$ , and the units of the preexponential factor are chosen so the rate is in mol/l-s. The pseudo first-order rate constant,  $k_{\text{eff}}$ , is then calculated from these parameters assuming the dependence on  $\text{CH}_4$  concentration is unity and the dependence on oxygen is zero at an initial fuel concentration of 0.003 mol/l. This procedure yields a  $k_{\text{eff}}$  for a comparable concentration to that used in Webley and Tester [3]. The low-temperature experiments covered both lean and rich conditions, but no oxygen concentration dependence was observed. In addition, no significant induction period was observed. A global fit to the high temperature data [3] gives an expression for the fuel consumption to be

$$-d[\text{CH}_4]/dt = k [\text{CH}_4]^{0.99} [\text{O}_2]^{0.66} \quad (3)$$

and  $k = 10^{11.1} \exp(-21500/T)$ . However, Webley and Tester also provide a calculation for a pseudo first-order rate constant, calculated from the same data. The fitted values for that expression are used here for  $k_{\text{eff}}$ .

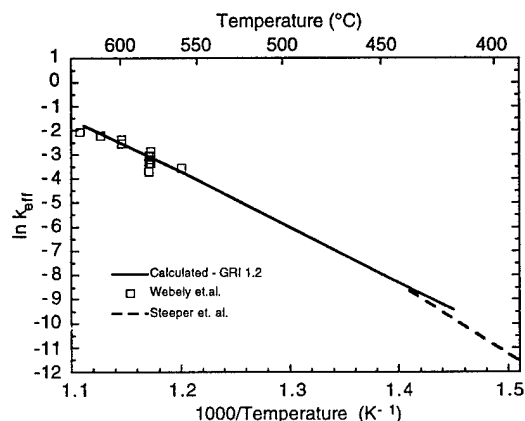


Figure 1. Comparison of calculated effective first order rate constants for the oxidation of methane from the GRI 1.2 mechanism and experimental results.

The agreement of the Chemkin calculation using the unmodified GRI mechanism with the experimental data is excellent. Although the calculation reveals fuel consumption curves that exhibit a brief induction period, it is a small fraction of the  $1/e$  time constant. The GRI 1.2 mechanism can accurately reproduce the available fuel consumption rates for the oxidation of methane over the entire temperature range likely to be used in SCWO applications.

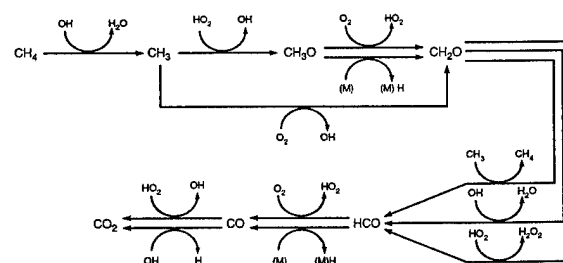
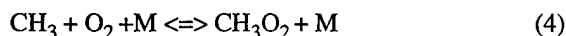


Figure 2. Flux diagram of the major carbon species in the oxidation of  $\text{CH}_4$  at 500 °C and 25.0 MPa in supercritical water predicted by the GRI 1.2 mechanism.

Fig. 2 shows a qualitative view of the pathway of methane conversion to  $\text{CO}_2$  in the model. Only a very small fraction of the  $\text{CH}_3\text{O}$  is converted to methanol by reaction with water, so this path does not appear in the figure. In addition, because

methanol is significantly more reactive than methane, it is not accumulated. In fact, no significant amount of transient non-radical species are accumulated, other than CO and CO<sub>2</sub>. This is in contrast to the results for methanol oxidation where formaldehyde and hydrogen peroxide are produced in significant quantities.

Fig. 3 shows a more complicated flux diagram for the oxidation of methane using a mechanism [5] that includes the formation of CH<sub>3</sub>O<sub>2</sub> by the reaction



The route by which methane is oxidized is very different if this key reaction, and the subsequent reactions of CH<sub>3</sub>O<sub>2</sub> as an oxidizer with fuel species, are included. These reactions are not included in the GRI mechanism.

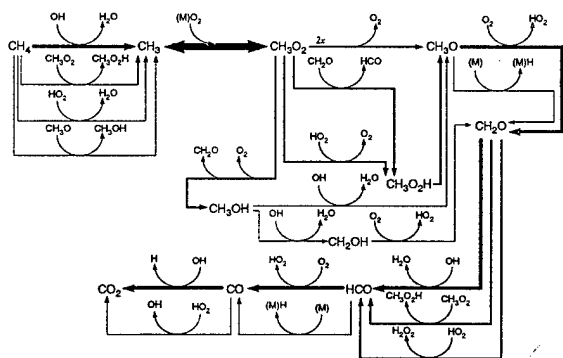


Figure 3. Flux diagram of major carbon species in the oxidation of CH<sub>4</sub> at 500 °C and 25.0 MPa in supercritical water predicted by the mechanism described in Schmitt et al.

The performance of the GRI mechanism at these conditions can be evaluated on aspects other than fuel consumption rates. The global fit from Ref. 3 suggests that there is an oxygen concentration dependence of order 0.66. Table 1 shows GRI mechanism predictions for varying the equivalence ratios at constant fuel mole fraction of 0.0005 at 600 °C. The calculation reveals an oxygen concentration exponent of 0.734, in acceptable agreement with the data. However, this O<sub>2</sub> dependence is preserved at lower temperature in contrast to the experimental results from Steeper et. al. In contrast, the same calculation using the Schmitt/Alkam model shows essentially no dependence on oxygen concentration. The inclusion of the rapid equilibrium with O<sub>2</sub> in the Schmitt/Alkam model serves to remove any oxygen dependence from the mechanism. This suggests that the GRI mechanism, when compared to the low temperature data, is not fully representing the

additional pathways associated with temperatures below 450 °C.

O <sub>2</sub> mole fraction	Equivalence ratio	k <sub>eff</sub> (s <sup>-1</sup> ) <sup>a</sup>	Fitted k <sub>eff</sub> (s <sup>-1</sup> ) <sup>b</sup>
0.0133	0.075	0.256	0.294
0.00665	0.15	0.182	0.176
0.00400	0.25	0.132	0.121
0.00266	0.375	0.102	0.090
0.00133	0.75	0.0571	0.0542
0.00100	1.0	0.0438	0.0439
0.00067	1.5	0.0284	0.0327

Table 1. Effect of Oxygen Concentration on Rate of Methane Oxidation. Initial methane mole fraction = 5.0 × 10<sup>-4</sup>, T=600 °C, P=250 bar.

<sup>a</sup>Defined as k<sub>eff</sub> = 1/t, with reaction time, t, at [CH<sub>4</sub>]/[CH<sub>4</sub>]<sub>0</sub> = 1/e. <sup>b</sup>Prediction from fit to k<sub>eff</sub> = a(O<sub>2</sub> mole fraction)<sup>b</sup>, with a = 7.02 and b = 0.734

It is possible that the GRI mechanism is appropriate at higher temperature, but it appears that the methylperoxyl chemistry must be included at lower temperature. This may be the origin of the slightly higher rates calculated at the lowest temperatures in Fig. 1.

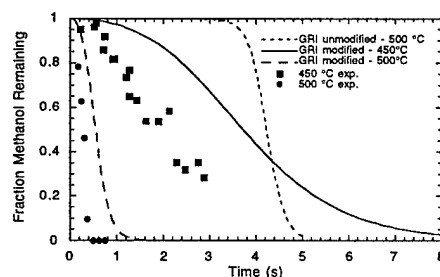
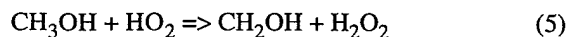
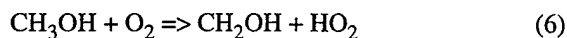


Figure 4 Comparison of experimental results from methanol oxidation at 450 °C and 500 °C at 27 MPa with the predictions from the GRI 1.2 mechanism with and without the addition of Reactions 5 and 6. The unmodified calculation shows essentially no reaction at 450 °C.

Recently our lab has measured the oxidation of methanol and the simultaneous production of formaldehyde at 440 - 500 °C [12]. Fig. 4 shows a comparison of the rate of methanol disappearance predicted from the GRI mechanism and this experimental data. The agreement between the GRI mechanism and the measurements is poor. This is primarily because the mechanism lacks the key reactions



and



The role of Reaction 6 is not particularly significant at hydrothermal conditions, but without Reaction 5, an unreasonable induction period is calculated. Fig. 4 also shows the results from a calculation when these steps, and reverse reactions, are added to the scheme with the following parameters used for Reaction 5:  $A_f = 3.98 \times 10^{13}$ ,  $E_{a_f} = 19.4$  kcal/mol,  $b_f = 0.00$ ,  $A_r = 3.13 \times 10^{15}$ ,  $E_{a_r} = 10.75$  kcal/mole,  $b_r = -0.90$ ; where f and r refer to the forward and reverse reactions, and  $k = A \exp T^b (E_a/RT)$ . Agreement with the data is greatly improved, although does appear to be still about two times slower. Note however, that at these conditions, this difference in rate corresponds to a temperature difference of about 10 °C. The results from the calculation also show good quantitative agreement for th4 formation of formaldehyde as an intermediate at concentrations up to 18% of the initial methanol mole fraction.

### Conclusions

The recently developed GRI 1.2 methane oxidation mechanism has been applied to the oxidation of methane and methanol by oxygen in water at 25 MPa and temperatures ranging from 400 - 630 °C. These conditions deviate substantially from the much higher temperature and lower pressure conditions at which it was designed and optimized. The results for the oxidation of methane with no modification of the mechanism agree very well with the available experimental results at these conditions. However, there is some evidence that the mechanism may be incomplete when applied to the <450 °C range; perhaps because the GRI mechanism does not contain  $\text{CH}_3\text{O}_2$  chemistry. To represent properly the oxidation of methanol and the formation of formaldehyde, the simple addition of one reaction to the mechanism was required. With this modification, good agreement was achieved in the temperature range of 440 °C to 500 °C.

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